 **Europäisches Patentamt**  
**European Patent Office**  
**Office européen des brevets**

**(11) Publication number: 0 223 908 A2**

**(12) EUROPEAN PATENT APPLICATION**

**(21) Application number: 86107597.6**

**(51) Int. Cl. 4: D 04 H 1/64**

**(27) Date of filing: 04.06.86**

**(30) Priority: 18.11.85 JP 256594/85**

**(43) Date of publication of application:  
03.06.87 Bulletin 87/23**

**(84) Designated Contracting States:  
DE FR GB IT**

**(71) Applicant: Nakazawa, Tomio  
27-3, Minamienokicho Shinjuku-ku  
Tokyo(JP)**

**(72) Inventor: Nakazawa, Tomio  
27-3, Minamienokicho Shinjuku-ku  
Tokyo(JP)**

**(74) Representative: Boeters, Hans Dietrich, Dr. et al,  
Boeters, Bauer & Partner Thomas-Wimmer-Ring 14  
D-8000 München 22(DE)**

**(54) Process for continuous production of nonwoven highly water-absorbent complex.**

**(57) The invention relates to a process for the continuous production of nonwoven highly water-absorbent complex characterized in adding in advance to an aqueous monomer solution a crosslinking agent and a oxidizing polymerization Initiating agent having a latent activity, and after impregnating a continuous nonwoven fibrous web with this solution, causing a rapid polymerization reaction by adding an activator to this web so as to form a water-swelling polymer in this web, thereby continuously forming a nonwoven highly water-absorbent comple. As the radical polymerization initiator a peroxide e.g. hydrogen peroxide is used, and as the activator a water soluble reducing agent capable of forming a redox system with said peroxide, e.g. aniline or sodium sulfite is used.**

- 1 -

## DESCRIPTION

PROCESS FOR CONTINUOUS PRODUCTION OF  
NONWOVEN HIGHLY WATER-ABSORBENT COMPLEXTECHNICAL FIELD

The present invention relates to a process for the continuous production of a nonwoven highly water-absorbent complex used as a humor absorbent, including paper diapers and sanitary articles.

BACKGROUND OF THE PRIOR ART

As a prior art of the present invention, an absorbent complex produced by irradiation is disclosed in International Application No. PCT/US81/00601 (W081/03274). More specifically, after applying an aqueous acrylic acid or methacrylate solution to a fibrous substrate, an attempt is made to obtain an absorbent complex by applying electromagnetic radioactive rays or fine-particulate ionization radioactive rays to this material so as to convert the acrylic acid or methacrylate into a water-swelling polymer. Since a monomer can be used directly, this

- 2 -

method is epoch-making in comparison with the conventional art in which powdered polymer is mixed with wood pulp and the like (see Japanese Patent Publication No. 53-46199).

5           However, the aforementioned prior art has drawbacks in that (1) since a self-crosslinking reaction is carried out, the water-absorption properties of a complex obtained are inferior to those of a particulate water-absorbent polymer; (2) large-  
10   scale and highly expensive apparatuses including an electron beam accelerator are required, and the process thereof also becomes complicated, with the result that the amount of investment needed becomes large; and (3) the amount of residual monomers is large.

15           The problem of the invention is, therefore, to overcome the drawbacks of the prior art by providing a process for producing a nonwoven complex having excellent water-absorption properties continuously at high speed.

20   BRIEF SUMMARY OF THE INVENTION

This problem is solved according to the present

- 3 -

invention by adding in advance to an aqueous monomer solution a crosslinking agent and an oxidizing radical polymerization initiating agent having a latent activity, and after impregnating a continuous nonwoven fibrous web with this solution, causing a rapid polymerization reaction by adding an activator (i.e. an oxidizing agent or a reducing agent) to this web so as to form a water-swelling polymer in the web, thereby continuously forming a nonwoven highly water-absorbent complex.

#### BRIEF DESCRIPTION OF THE DRAWING

Fig.1 is a flow sheet briefly showing the process of the present invention.

#### DETAILED DESCRIPTION OF THE INVENTION

More detailed description will be made hereinafter with reference to a flow sheet shown in the attached drawing.

##### (1) Nonwoven Continuous Fibrous Web

In terms of properties, it is necessary for a nonwoven fibrous web to be bulky and porous as

well as outstanding in compression recovery. Accordingly, the nonwoven fibrous web should desirably have an apparent density of 0.05 g/cm<sup>3</sup> or below (preferably 0.002 to 0.02 g/cm<sup>3</sup> ) and a compression recovery rate\* of 80% or above.

To obtain the web having such properties, polyester, polypropylene, or polyethylene hydrophobic fibers having a fineness of 3d or above (preferably 4 to 10d) and a hollow and irregular-shaped cross section are used. To prepare a nonwoven web from these fibers, a 20 to 60 g/m<sup>2</sup> parallel web and a random web are formed from a fibrous mixture by the use of the card process, the air laid process, or other similar process. Subsequently, these webs are treated in a cylindrical drier or other heat treatment apparatus at a temperature of 150 to 250 °C so as to couple the fibers.

\*Compression Recovery Rate (R) :

$$R (\%) = \frac{2V_{0.5} - V_1}{1V_{0.5} - V_1} \times 100$$

1V<sub>0.5</sub> = the bulk (mm) of a sample web

- 5 -

when it is treated for 10 minutes  
under a light load of  $0.5 \text{ g/cm}^2$ .

5        V1 = the bulk (mm) of a sample web  
         when it is treated for 5 hours  
         under a heavy load of  $50 \text{ g/cm}^2$ .

10       2V0.5 = the bulk(mm) of a sample web  
         when a light load of  $0.5 \text{ g/cm}^2$   
         is applied to it for 10 minutes  
         after being left for 30 minutes  
         as it is on measurement of V1.

(2) Polymeric Monomer

15       A monomer used in the present invention is  
         an acrylic acid or one essentially constituted by  
         the same, and 50% or more thereof is preferably  
         neutralized by an alkali metallic salt, e.g. a  
         sodium salt or a potassium salt. In view of the  
         subsequent dehydrating process, the higher the  
         concentration of the monomer, the greater the  
         economic efficiency, with the result that it is  
20       advantageous to set the concentration of the  
         monomer to the vicinity of saturation solubility  
         in a working temperature.

### (3) Crosslinking Agent

One of the characteristic features of the present invention is the use of a crosslinking agent, which proves extremely advantageous in controlling the properties of the polymer and makes it possible to widen the range of selection of reaction conditions in comparison with the self-crosslinking type employed in the prior art.

The crosslinking agent is selected from compounds having properties of copolymerization with an acrylic monomer, compounds having reactivity with a functional group of an acrylic acid monomer, or compounds having the properties of both of these two types of compounds. Typical examples of this crosslinking agent are ethylene glycol bis-acrylate, N,N-methylene bis-acrylamide, ethylene glycol glycidyl ether and N-methylolacrylamide. The amount of the crosslinking agent to be added is preferably 0.1% to 3% by weight of the polymeric monomer. If the amount is too small, a problem arises in the stability of the gel: if too large, the water-absorbing capability decreases.

- 7 -

#### (4) Oxidizing Radical Polymerization Initiator

The radical polymerization initiator employed in the present invention must be such as to be capable of forming a redox system with an amine and a reducing agent which have a certain degree of solubility with respect to a monomer or water and must exhibit oxidizing properties. As radical polymerization initiators having such properties, it is possible to use peroxides, e.g. hydrogen peroxide, persulfates such as ammonium persulfate and potassium persulfate, and hydroperoxides such as t-butyl hydroperoxide and cumene hydroperoxide.

For instance, a water soluble radical polymerization initiator of azo type, which has no oxidizing properties, cannot form a redox system with an amine or reducing agent; therefore, it cannot be used in the present invention.

Incidentally, the amount of the radical polymerization initiator used is preferably 0.1 to 2% by weight of the monomer.

#### (5) Activator



An activator capable of causing polymerization reaction rapidly in a predetermined period of time should form a redox system with the aforementioned oxidizing radical polymerization initiator. For instance, one or more of the following may be used: amines, e.g. aniline, monoethanol amine, diethanol amine, triethanol amine and dimethyl aniline; and water soluble reducing agents, e.g. sodium sulfite, sodium hydrogensulfite, sodium thiosulfate, copper sulfate, ferrous sulfate, and L-ascorbic acid and salts thereof, erysorbic acid (isoascorbic acid) and salts thereof, polyphenols, such as gallic acid, and derivatives thereof. The amount of the activator added is preferably 0.01 to 4% by weight of the monomer.

(6) Conditions for Polymerization Reaction

As described above, the nonwoven fibrous web containing, the mixed solution of the monomer, the crosslinking agent and the oxidizing radical polymerization initiator causes a rapid polymerrisation reaction with the addition of the activator. In view of te fact that this is a continous process, the web containg the mixed

- 9 -

solution should be stable for a long time before the activator is added. After the addition of the activating agent, the rapid polymerization reaction should take place and be completed within a short time. In addition, a highly water-absorbent polymer having a sufficient water-absorbing capability should be formed stably in the nonwoven fibrous web. Described below are the desirable conditions for this polymerization reaction.

(i)

The Amount of Mixed Monomer Solution to be Adhered to the Nonwoven Web.

The mixed monomer solution is adhered to the nonwoven web by means of impregnation, coating or spraying. The amount of the mixed monomer solution to be adhered and the conditions of adhesion vary according to the complex to be obtained, but the rate of pickup is normally 1 to 20 weight parts with respect to 1 weight part of the web.

(ii)

Conditions of Addition of Activator.

When adding the amine or the reducing agent,

- 10 -

it is advantageous to use the same as it is or in the form of an aqueous solution if it is a solution, or if it is a solid, it should be used in the form of an aqueous solution containing it.

5 It is effective to spray a predetermined amount of it onto the monomer-containing web, and it is desirable to spray it onto both sides of the web as uniformly as possible.

(iii)

10 Adjustment of Polymerization Reaction Time.

The adjustment of polymerization reaction time is depending on the following factors:

- a. The concentration and temperature of the monomer to be mixed in the web.
- 15 b. The amount of polymerization heat generated.
- c. The concentration and temperature of the activating agent.
- d. The ambient temperature of a reaction tank at the time of polymerization reaction.

20 However, it is a general practice to adjust the polymerization time by controlling the temperature

- 11 -

of the reaction tank described in d above.

It is possible to control the polymerization reaction time between 5 sec. to 1 hour by selecting the conditions a, b, c and d above.

5 However, it is desirable to complete the polymerization reaction within 20 sec., preferably 10 sec., by maintaining the temperature of the reaction tank at 50 to 120 C.

(7) Post-treatment of the Complex

10 With respect to the web for which polymerization is completed, post-treatment, including drying for controlling the residual moisture content, softening treatment, or lamination bonding with wooden pulp layers by  
15 making use of the residual moisture content, is carried out before effecting a final winding-up process so as to produce the nonwoven highly water-absorbent complex. The complex thus  
20 obtained is cut into a predetermined size, or folded, and can be used as the inner absorbent for disposable diapers for infants, the absorbent for diapers for adults, or the absorbent for sanitary napkins, or, in some cases, as the absorbent for construction material and the like.

- 12 -

As described above, according to the present invention, the following advantages can be obtained: (1) since the polymerization speed is high, continuous production can be effected easily, and it is possible to use compact apparatuses for production; (2) since the reaction is carried out uniformly, it is possible to effect the production under smooth and stable operating conditions, and (3) the degree of crosslinking and the degree of polymerization can be controlled.

#### BEST MODE FOR CARRYING OUT THE INVENTION

The following examples describe the present invention, although these should not be considered as a limitation to the object of the present invention.

##### Example 1

###### 1) Preparation of Web

A 50 g/m<sup>2</sup> web was formed from 70% of 6d x 51 mm hollow polyester fibers (made by Teijin Co., Ltd.) and 30% of 3d x 51 mm heat-fusible polypropylene conjugated fibers (made by Chisso Co., Ltd.) using a card. The web was subsequently

- 13 -

led into a heat treatment apparatus (made by Honeycomb Co., Ltd.) heated to 220 °C and a nonwoven fabric having the following properties was produced.

5	basis weight:	40 g/m <sup>2</sup>
	thickness:	8 mm
	apparent density:	0.005 g/cm <sup>3</sup>
	compression recovery rate:	90 %

## 2) Preparation of Mixed Monomer Solution

10           A 40 % aqueous sodium hydroxide solution and pure acrylic acid (made by Sumitomo Chemical Co., Ltd. and conforming to JIS) were mixed in a water-cooled tank having a capacity of 40 litres, and sodium acrylate solution having a neutralization  
15           rate of 80 % and a monomer concentration of 42 wt.% was prepared. N, N-methylene bis-acrylamide was then dissolved in this solution in a proportion of 0.2 % by weight of the monomer. Then, as the oxidizing radical polymerization  
20           initiator, potassium peroxide was dissolved in said solution in a proportion of 0.3 % by weight of the monomer. This mixed monomer solution was adjusted at 60 °C through a heat exchanger and was then introduced into a roll coater.

- 14 -

### 3) Impregnation of Nonwoven Fabric with Mixed Monomer Solution

The aforementioned nonwoven fabric was impregnated with the mixed monomer solution on both sides thereof by a double roll coater such that a pickup rate of 1000 wt.% was achieved.

### 4) Polymerization Reaction

The above-described impregnated nonwoven fabric was let onto a stainless conveyor, and as the reducing agent a 7 % aqueous sodium hydrogensulfite solution heated to 50 °C was adhered uniformly to a sheet from above using a spray. This resulted in polymerization reaction accompanying sudden generation of heat. The impregnated nonwoven fabric was then passed in a falling state through the reaction tank in such a manner as to oppose the flow of air heated to 120 °C and the polymerization reaction was completed in approximately 10 seconds, and it was possible to obtain a complex containing a highly water-absorbent polymer solidified in the nonwoven fabric. This complex was then passed through a drier and dried to a moisture content of 10 %.

### 5) Performance of Complex

- 15 -

The physiological saline absorbing capacity of this complex was 55 and the residual monomer was approximately 100 ppm. The weight of the complex was 200 g/m<sup>2</sup>.

- 5       \*\* Physiological saline Absorbin Capacity;  
           1 g of the complex is placed in a 500 ml  
           beaker, 300 g of 0.9 wt.% physiological  
           saline solution is added, and the mixture is  
           left as it is for 2 hours. After that the  
 10       mixture is filtered by a 100-mesh filter,  
           and the physiological saline absorbing  
           capacity is calculated by the following  
           formula;

Physiological Saline Absorbing Capabilty=

$$15 \quad \frac{\text{amount of physiological(g)} - \text{amount filtered (g)}}{\text{saline solution}} \\ \text{complex (g)}$$

### Example 2

#### 1) Preparation of Web

- 20       A carded web was made of 80% of 8d x 51 mm  
           hollow conjugated polyester fibers (made by  
           Mitsubishi Rayon Co., Ltd.) and 20% of 3d x 51 mm



- 16 -

polyester heat-fusible fibers (marketed by Uni-Chika Co., Ltd. under the reference Melty).

This web was led continuously into an oven wherein 250°C heated-air was circulated, and it was

5 possible to obtain a nonwoven fabric in which heat-fusible fibers were melted and the web-constituting components bonded together. The properties of the nonwoven fabric were as follows:

10	basis weight:	30 g/cm <sup>2</sup>
	thickness:	5 mm
	apparent density:	0.006 g/cm <sup>3</sup>
	compression recovery rate:	85%

2) Preparation of Mixed Monomer Solution

15 A 70 wt.% aqueous potassium acrylate solution was prepared with the same apparatus as the one used in Example 1 under cooling condition, employing sodium hydroxide. The neutralization rate was 75%. N-methylene bis-acrylamide was then added to this aqueous monomer solution so that its

20 concentration would become 0.3% by weight of the monomer. Then, as the oxidizing radical polymerization initiator hydrogen peroxide was added to the mixed solution and was mixed so that its concentration would become 0.2% by weight of

the pure monomer.

3) Adhesion of Mixed Monomer Solution to the Nonwoven Fabric

5 A mixed monomer solution was adhered to one side of the aforementioned nonwoven fabric by the roll coater such that the pickup rate of about 500 wt.% was achieved.

4) Polymerization Reaction

10 The above-described monomer-adhered nonwoven fabric was passed in a falling state through the reaction tank heated to 100 °C. Subsequently, a 7% aqueous monoethanolamine solution was sprayed perpendicularly on the monomer-coated surface of the nonwoven fabric in the upper layer of the reaction tank, and the polymerization reaction was completed in approximately 15 minutes.

15 Consequently, it was possible to obtain a highly water-absorbent complex having a structure in which polymers having a larger particle size were distributed on one side of the nonwoven fabric.

20 5) Performance of Complex

Physiological saline absorbing capacity: 48  
residual monomers; trace

Example 3

150g/m<sup>2</sup> wooden pulp mat (NBKP made by Rayonier Co., Ltd.) was bonded to both sides of the complex obtained in Example 1 by applying water to the surface of the complex, and pressing was effected for this structure. This structure was cut into dimensions of 25 cm (height) x 33 cm (length). After removing the absorbent of a commercially available paper diaper, the structure was inserted into said paper diaper and a consumer test was carried out. It was found that the articles according to the present invention have doubled its rate of water absorption in comparison with commercially available ones. Thus, it was possible to obtain the absorbent in which the rate of occurrence of leakage was extremely low even without replacement at night.

CLAIMS

1. A process for the continuous production of a nonwoven highly water-absorbent complex wherein, after impregnating a nonwoven continuous fibrous web with an aqueous polymeric monomer solution consisting of an acrylic acid or essentially consisting of an acrylic acid, said polymeric monomer is polymerized, comprising continuously adding a uniform mixed solution obtained by adding to said aqueous polymeric monomer solution a soluble crosslinking agent and an oxidizing radical polymerization initiator having a latent activity such as to show in the presence of an activator a polymerization initiating action to said nonwoven continuous fibrous web having porosity and compression-resistant stability, and subsequently causing a rapid polymerization reaction by adding to said web said activator in order to activate said radical polymerization initiator, thereby forming a polymer in said fibrous web.
2. A process according to claim 1, wherein said radical polymerization initiator is a peroxide,

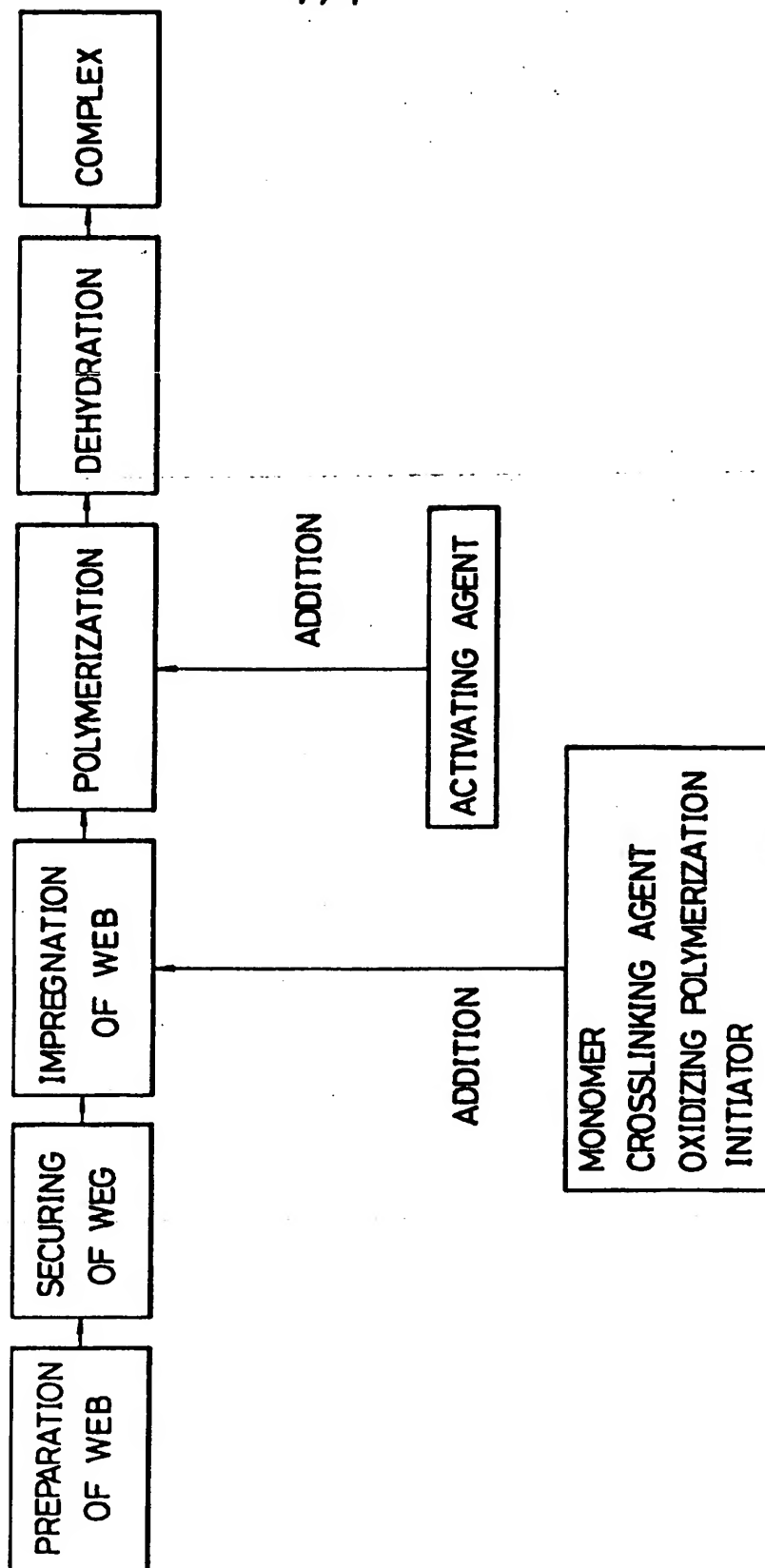
and said activator is an amine capable of forming a redox system with said peroxide.

3. A process according to claim 1, wherein said radical polymerization initiator is a peroxide, and said activator is a water soluble reducing agent capable of forming a redox system with said peroxide.

5

4. A process according to claim 1, wherein said nonwoven continuous fibrous web is made of hydrophobic synthetic fibers and has an apparent density of  $0.05 \text{ g/cm}^3$  or below.
5. A process according to claim 1, wherein said nonwoven continuous fibrous web is mainly composed of polyester fibers of 4d or above having a hollow and irregular-shaped cross section.

FIG.1



12

**EUROPEAN PATENT APPLICATION**

21 Application number: 86107597.6

51 Int. Cl.<sup>3</sup>: **D 04 H 1/64**

22 Date of filing: 04.06.86

30 Priority: 18.11.85 JP 256594/85

43 Date of publication of application:  
03.06.87 Bulletin 87/23

88 Date of deferred publication of search report: 12.07.89

84 Designated Contracting States:  
DE FR GB IT

71 Applicant: Nakazawa, Tomio  
27-3, Minamienokicho Shinjuku-ku  
Tokyo(JP)

72 Inventor: Nakazawa, Tomio  
27-3, Minamienokicho Shinjuku-ku  
Tokyo(JP)

74 Representative: Boeters, Hans Dietrich, Dr. et al,  
Boeters, Bauer & Partner Thomas-Wimmer-Ring 14  
D-8000 München 22(DE)

54 Process for continuous production of nonwoven highly water-absorbent complex.

57 The invention relates to a process for the continuous production of nonwoven highly water-absorbent complex characterized in adding in advance to an aqueous monomer solution a crosslinking agent and a oxidizing polymerization initiating agent having a latent activity, and after impregnating a continuous nonwoven fibrous web with this solution, causing a rapid polymerization reaction by adding an activator to this web so as to form a water-swelling polymer in this web, thereby continuously forming a nonwoven highly water-absorbent complex. As the radical polymerization initiator a peroxide e.g. hydrogen peroxide is used, and as the activator a water soluble reducing agent capable of forming a redox system with said peroxide, e.g. aniline or sodium sulfite is used.



European Patent  
Office

# EUROPEAN SEARCH REPORT

0223908  
Application Number

EP 86 10 7597

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
A	EP-A-0 019 169 (BASF) * Claims 1,4,5; page 3, line 1 - page 8, line 21; example 1 *	1-4	D 04 H 1/64
A	GB-A- 962 458 (RÖHM & HAAS) * Claims 1,2,4,8-10; page 1, line 15 - page 4, line 13 *	1	
A	WO-A-8 001 031 (DU PONT) * Claims 1,2; page 2, lines 29-96 *	5	
X,E	CHEMICAL ABSTRACTS, vol. 107, no. 16, 19th October 1987, page 84, abstract no. 135863g, Columbus, Ohio, US; & JP-A-62 97 979 (MITSUBISHI PETROCHEMICAL CO., LTD) 07-05-1987 * Whole abstract *	1-3	
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)
			D 04 H
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 18-04-1989	Examiner BLASBAND I.
<b>CATEGORY OF CITED DOCUMENTS</b> X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			



**This Page is Inserted by IFW Indexing and Scanning  
Operations and is not part of the Official Record**

**BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ BLACK BORDERS
- ☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☐ FADED TEXT OR DRAWING
- ☐ BLURRED OR ILLEGIBLE TEXT OR DRAWING
- ☐ SKEWED/SLANTED IMAGES
- ☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☒ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☐ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: \_\_\_\_\_

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.**